

NATURE OF THE CHEMICAL REACTION FOR FURFURAL MODIFIED ASPHALT

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INTRODUCTION

Three of the most serious problems of asphalt pavements today are rutting, cracking, and susceptibility to moisture damage (stripping). Asphalt manufacturers have been mixing asphalts with polymers to produce polymer-modified asphalts with improved rheological properties. However, the costs for these improved polymer-modified asphalts are almost double that of regular asphalts. FHWA researchers have found that asphalt modified by the chemical, furfural (which is prepared by simple elimination reaction of aldopentoses obtained from oat hulls), exhibited better stripping properties and was less temperature susceptible than the virgin asphalt,^{1,2} while costing less than polymer-modified asphalts. This paper discusses the possible structure of the furfural-modified asphalt, data for the virgin and furfural-modified asphalts and their Corbett fractions, data from a model reaction between phenol and furfural, and a possible explanation of this structure based on these data.

MATERIALS USED

An Alaskan North Slope asphalt (asphalt A5), obtained from the Strategic Highway Research Program (SHRP), was used. It is an AC-5 asphalt, SHRP number AAV. All of the reagents used were analytical grade from Baxter Scientific Products, McGraw Park, IL, unless otherwise specified.

EXPERIMENTAL METHOD

Furfural Reaction: The furfural-modified asphalt (asphalt A5F) was prepared from asphalt A5 according to the method described by Chollar, et al.² The model phenol-furfural product was prepared by continuously stirring phenol (10 g), furfural (10 g), and concentrated hydrochloric acid (0.19 ml) at 93.3°C for 90 min. The resulting product was analyzed by Thin Layer Chromatography (TLC), Fourier Transform Infrared (FTIR), and High Performance-Gel Permeation Chromatography (HP-GPC).

TEST METHODS

I. ASTM D-4124 (Corbett Analysis): ASTM D-4124 was used to fractionate asphalts A5 and A5F.

II. Thin Layer Chromatography (TLC): The residual furfural starting material in asphalts was detected by TLC using the Benzidine³ and 2,4-Dinitrophenyl hydrazine⁴ spot tests. Visual observation of the resulting colors both with and without ultraviolet (UV) radiation at 254 and 366 nm wavelength was used to detect/differentiate different compounds.

III.a. Reverse-Phase High Performance Liquid Chromatography (RP-HPLC): A Waters HPLC system was used for this study with a 600E brand work station. Methanol or tetrahydrofuran (THF) was used as a solvent at a flow rate of 1 ml/min. A 0.4 ml sample was always injected. Elution of the material was carried out by two methods in an isocratic mode: 1) eluting the sample with methanol for a 10 min period for detecting the furfural starting material, and 2) eluting the sample with methanol from 0 to 15 min, then with THF from 15 to 45 min, and then with methanol from 45 to 61 min to observe the changes which occurred in asphalt A5 and A5F Corbett fractions.

The following procedure was used to determine the starting material (furfural) in Corbett fractions of asphalt A5F by an HPLC technique using reverse-phase chromatography.

1. Asphalt (A5 or A5F, 10mg) was dissolved in 4 ml of 1:1 THF/methanol. The resulting solution was passed through a wet (methanol) Sep-pak C₁₈ cartridge (a reverse phase HPLC technique to rapidly clean the asphalt sample and preserve the life of the RP-HPLC column) and collected. The solution from the Sep-pak was used to obtain the sample for RP-HPLC.
2. THF (2 ml) was passed through the Sep-pak. The solution was

collected in a separate vial. This fraction was used for further investigation.

3. Methanol (2 ml) was passed through the Sep-pak. The solution was collected and used for further investigation.
4. Methanol (2 ml) was again passed through the Sep-pak. The solution was collected in a fourth vial for further investigation.

A calibration curve was made by using different concentrations of furfural in methanol (1, 0.5, 0.25 and 0.125 percent). The solution (0.4 ml) was injected into the HPLC, using method #1 for 10 min in a isocratic mode, eluting in methanol. The peak area for the furfural signal was found at a retention time of 4.85 min and at a wavelength of 252 nm.

III.b. High Performance Gel Permeation Chromatography (HP-GPC): The sample preparation for HP-GPC and the method⁵ used was made according to the method reported by Memon, et al.

EXPERIMENTAL PROCEDURE

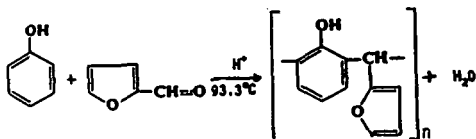
Nuclear Magnetic Resonance (NMR) Spectroscopy: Asphalt samples were dissolved in deuterated chloroform in a concentration of 10 percent (W/V). These were transferred to NMR tubes and were run for ¹H- and ¹³C analysis. A standard coaxial tube containing tetramethylsilane (TMS) was used as a standard.

Three different techniques were used to detect the aromatic/aliphatic carbon and proton ratio and non-protonated carbon atoms present in asphalts A5 and A5F and their polar aromatic and naphthene aromatic fractions: conventional ¹H-, ¹³C distorless enhancement polarization transfer (DEPT), and gated decoupling without nuclear overhauser effect (NOE) ¹³C-NMR.

Fourier Transform Infrared (FTIR) Spectroscopy: The asphalts A5 and A5F were run on a FTIR using neat thin films on a sodium chloride (NaCl) plate. The Stokes analysis⁶ was used to calculate and compare peak areas and ratios to each other in a spectrum. Ratios used for this comparison are shown in figure 10. It has been shown that the 1378-1578 cm⁻¹ region (aliphatic region) does not change significantly for most asphalts including A5 and A5F. Thus, ratios of this aliphatic region to other infrared peak regions for asphalt (A5) will show the increase or decrease in that regional area as compared to the same ratio for asphalt (A5F).

RESULTS

There are several ways in which furfural can react with the phenolic type compounds in asphalt. One of the most probable ways that furfural can react with phenol is by a condensation type of reaction. The model for this is:



We think that this is the type of reaction that is occurring in the furfural-asphalt modification and that this is the type of product that is observed in asphalt A5F. The following data is obtained in support of this product:

1. **Increase of polarity.** Table I gives the Corbett analyses of asphalts A5 and A5F. There is a significant increase in asphaltene (highly polar) and a slight decrease in the polar and naphthene aromatic fractions of the furfural-modified asphalt. Table II gives the results of the TLC analyses of asphalts A5 and A5F. There are changes occurring in the polar and naphthene aromatic fractions using 90 percent methanol - 10 percent toluene. There were no other changes in the other fractions. Therefore, a reaction occurs with a change in the polar and naphthene aromatic fractions of the asphalt. These results show the higher polarity of asphalt A5F.

2. **Furfural consumption.** a. The detection of furfural in the furfural-asphalt reaction was attempted by mixing different amounts of furfural (0.5, 0.38, 0.13, 0.06 and 0.03 ml) in hot asphalt A5 (50 gms) at 57°C on a hot plate for 30 s and observing the separation of the mixtures by RP-HPLC. No signal was observed at 252 nm wavelength (wavelength of the pyrrole ring with the 2-CHO

functional group in furfural) at a retention time of 4.85 min (figure 1, furfural in asphalt at 57°C). Therefore, no free furfural is found in any of the mixtures. b. The detection of furfural was also attempted by mixing different amounts of furfural (0.5, 0.38, 0.13, 0.06 and 0.03 ml) in 50 grams of warm asphalt A5 (26.7°C). The furfural-asphalt mixture (100-150 mg) was analyzed by the above procedure using RP-HPLC. Unreacted furfural was observed in all mixtures at 252 nm wavelength after 4.85 min retention time (figure 1, furfural in asphalt at 26.7°C). c. Asphalt A5 (50 g) was mixed with furfural (0.5 ml) at room temperature. Reverse-phase HPLC was used to analyze this mixture using the above procedure. Figure 1 (furfural in methanol) shows that at 4.85 min, the free furfural signal appeared. The mixture was then heated at 57°C for 30 s and analyzed. There was no furfural signal detected at that time. Thus, the reaction uses furfural and proceeds at temperatures above 27°C. d. The detection of furfural was attempted with asphalts A5 and A5F and their Corbett fractions using the sample preparation method above. These solutions were analyzed by the above reverse-phase method (method #2) and the results are reported in table III. There is no absorption observed at 252 nm in the three fractions of asphalt A5 and A5F at any retention time. These data indicate that furfural has been used in the furfural-asphalt A5 reaction and is not found in any of the Corbett fractions of asphalt A5F.

3. The reaction converts phenolic compounds into substituted phenolic compounds. Rao⁸ has reported that substitution of an -OH group on benzene will give a signal at 270 nm wavelength. A disubstituted benzene shows a signal at 276 nm. O-catechol is an example of this shift, showing a transition at 276 nm. A trisubstituted benzene molecule shows a transition at 287 nm wavelength. The RP-HPLC data for the naphthene aromatic fraction of asphalt A5 shows a small broad signal at 272 nm (table III and figure 2) with 4.7 min retention time in THF followed by methanol (solvent system). This signal may be due to phenol. When the corresponding asphalt A5F fraction was examined, no such signal was detected. This is an indication that a reaction is occurring with phenolic compounds. When the polar aromatic fraction of asphalt A5F was analyzed, a signal at 278 nm was observed in this polar aromatic fraction of asphalt A5F having a retention time of 4.7 minutes in methanol. This signal is possibly the monosubstituted phenolic material (table III).

4. The formation of more polymeric compound of higher molecular size. The GPC data were calculated according to published procedures by P. W. Jennings¹⁰ and reported as percent large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS), for each asphalt fraction. From the GPC data (table IV), it is clear that there is no significant change in the LMS, MMS, and SMS of asphalt A5F as compared to that of the asphalt A5. Thus, it is not apparent from the analysis if a reaction occurs. Furthermore, table IV demonstrates that the asphaltene fraction of asphalt A5F shows a decrease in LMS and an increase in MMS and SMS as compared to that of the asphaltene fraction of asphalt A5. The data also shows that there is a significant increase in LMS of polar aromatic fraction of asphalt A5F (4%). There is an increase in MMS of naphthene aromatic fraction (0.5%) of asphalt A5F. Thus, significant increases occurred only in the LMS of the polar aromatic fraction of the modified product. Figure 3 shows the changes observed in retention times obtained by RP-HPLC analysis of the naphthene aromatic and polar aromatic fractions of asphalts A5 and A5F. (The TLC analysis confirmed that changes occurred in only the naphthene and polar aromatic fractions). The asphaltene fractions of asphalts A5 and A5F have retention times of 16.5 and 16.8 minutes respectively. This means that there is no significant change in the LMS of the modified asphaltene fraction. The polar aromatic fraction of asphalt A5 begins around 19.5 min, whereas the corresponding asphalt A5F fraction begins around 15.5 min as shown in figure 3. This is an indication that the polar aromatic fraction of asphalt A5F has LMS materials appearing earlier than the corresponding fraction of asphalt A5. The spectrum of the naphthene aromatic fraction of asphalt A5 begins at around 20 min retention time, whereas the spectrum of the same fraction of asphalt A5F begins around 17 min retention time. Again, LMS compounds of the furfural-modified product appear earlier.

The ultraviolet spectra of the SMS of the polar aromatic fractions of asphalts A5 and A5F are in figure 4 and those of the LMS of the polar aromatic fraction of asphalts A5 and A5F are in

figure 5. The spectrum for the asphalt A5 (Figure 4) only shows a signal for phenols at 270 nm. The spectrum for the asphalt A5F fraction only shows a signal at 277 nm (figure 4). This shows the formation of a monomeric monosubstituted phenolic material in the furfural-modified asphalt. Figure 5 shows the presence of tri- or polysubstituted phenolic material of large molecular size (LMS region) in the polar aromatic fraction of asphalt A5F at 288 nm, whereas, there is no such signal in virgin polar aromatic fraction. Thus, it is possible that the furfural-asphalt reaction involves a substitution on the phenol ring in the form of a monomer in the SMS region as well as a polymer in the LMS region appearing in the polar aromatic fraction of asphalt A5F. Substituted phenolic types of compounds showing signals at 277 nm were also observed in SMS of asphaltene as well as naphthene aromatic fractions of furfural-modified asphalt.

The direct reaction between phenol and furfural was conducted under the same conditions as mentioned above. The GPC data shows that this reaction is a polymerization reaction, but it is a mixture of a monomer and a polymer, as is shown in figure 6. The GPC data shows that the model polymer product starts appearing around 22 min retention time, with peaks at 24.1, 28.3 and 30.6 min. A standard pyrene (molecular weight 202, about the weight of the monomer of phenol and furfural), appears around 29 min retention time. The molecular weight of the dimer of the furfural-phenol reaction is 346 and would be expected to be eluted around 27 to 28 min. Thus, the model reaction affords a polymer larger than that of this monomer, a material the same size as the dimer, and a material similar in size to the monomer.

These data showed that there are more large molecular size materials in the polar and naphthene aromatic fractions of asphalt A5F than there are in asphalt A5. These LMS materials in the polar aromatic fraction contain tri- or polysubstituted polymeric phenols. The SMS materials of the naphthene aromatic, polar aromatic, and asphaltene fractions contain monosubstituted monomeric phenols. The model reaction affords a polymer larger than that of the dimer, and a monomer of the size similar to that of the dimer of phenol and furfural. Since the model polymer was prepared under the same conditions as the furfural asphalt reaction, we can assume that furfural is reacting in the same way as the model polymer to give the same type of products.

5. Increase of aromaticity. Using the ^{13}C -NMR gated decoupling technique without NOE, NMR shows a 12 percent increase of aromatic carbon content in the polar aromatic fraction of asphalt A5F versus that of asphalt A5 (figure 7). The proton NMR spectrum of the polar aromatic fraction of asphalt A5F shows a 2 percent higher ratio of aromatic to aliphatic versus that of the polar aromatic fraction of asphalt A5 (figure 9). The infrared data (figure 10) show that the ratio of total aromatic to aliphatic content of asphalt A5F (10/5) is more than that of asphalt A5; the aromatic content of the furfural-reaction product has increased. The infrared data show that the ratio of monomeric to polymeric aromatic content of asphalt A5F (3/1) is less than that of asphalt A5, thus the polymeric substitution of the aromatic ring of the asphalt A5F has increased. These data show that the aromaticity of the asphalt A5F is higher than that of asphalt A5. Therefore, the phenolic groups in asphalt A5 are combining with furfural to produce a higher aromatic material (asphalt A5F) as suggested by the model structure.

6. Increase of non-protonated carbon atoms. Using the effect of the DEPT technique, ^{13}C -NMR showed an increase in the non-protonated carbon atom content of the polar aromatic fraction of the furfural-modified asphalt versus that of asphalt A5 (figure 8). The model structure of the modified product has more non-protonated carbon atom content than that of phenol or phenolic material reactants.

7. Increase of unsaturation. Infrared data (figure 10) show that the ratio of unsaturated to aliphatic content of asphalt A5F (4/5) is higher than that of asphalt A5. As a result, the unsaturated content of asphalt A5F has increased. With the addition of furfural, the model structure of the modified product contains more unsaturated carbon content than that of phenol or phenolic material reactants.

CONCLUSIONS

We have shown that our data for asphalt A5F using the above seven experimental results are consistent with the proposed structure of

the phenol-furfural polymeric product, and that it is possible that the furfural-asphalt reaction for phenolic materials in asphalt A5 is occurring in the same way as is proposed in the model reaction.

FHWA researchers will now pursue other reactions of this type to further improve the properties of asphalts.

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TABLE I: CORBETT ANALYSIS

Sample name	Asphaltene ± SD %	Polar Aromatics ± SD %	Naphthene Aromatics ± SD %	Saturates ± SD %
Asphalt A5	12.0 ± 1.6	28.3 ± 1.5	41.9 ± 0.1	12.7 ± 1.8
Asphalt A5F	18.3 ± 1.5	27.0 ± 1.9	38.8 ± 0.9	12.2 ± 0.4

Asphalt A5 = Virgin asphalt A5

Asphalt A5F = Furfural modified asphalt A5

TABLE II: THIN LAYER CHROMATOGRAPHIC COMPARISONS OF THE CORBETT FRACTIONS OF ASPHALT A5 AND A5F.

Functions	Asphaltene Fractions	Polar Aromatic Fractions	Naphthene Aromatic Fractions	Saturate Fractions
Observation	same	different	different	same
R _f of A5	same
R _f of A5F	same	0.05 0.55	0.21	

A5 = Virgin asphalt A5

A5F = Furfural modified asphalt A5

R_f = Retardation factor

..... = Not observed

TABLE III: RP-HPLC DATA FOR FURFURAL IN ASPHALT A5 AND ASF AND IN THEIR FRACTIONS

Reten. Time	A5-A-MT	ASF-A-MT	A5-A-M	ASF-A-M	A5-A-TM	ASF-A-TM	A5-A-T	ASF-A-T
4.7MIN	---	225 nm	--	205 nm 235 nm 244 nm	-- no signal --	--	210 nm 215-227 nm 248 nm 262 nm	210 nm --
6.5MIN	202 nm -- 230 nm 260 nm	-- 218 nm -- 260 nm	--no signal --	--	-- no signal --	--	200 nm 233 nm 242 nm 265 nm	-- -- 245 nm --
	AS-PA-MT	ASF-PA-MT	A5-PA-M	ASF-PA-M	AS-PA-TM	ASF-PA-TM	AS-PA-T	ASF-PA-T
4.7MIN	202 nm	202 nm	210 nm --	-- 278 nm	--	205 nm	--	202 nm
6.5MIN	202 nm	202 nm	-- no signal --	--	--	203 nm	240 nm	--
	AS-NA-MT	ASF-NA-MT	A5-NA-M	ASF-NA-M	AS-NA-TM	ASF-NA-TM	AS-NA-T	ASF-NA-T
4.7MIN	-- 209 nm -- 222 nm 264 nm	201 nm -- -- 222 nm 264 nm	209 nm	209 nm	220 nm 240 nm 272 nm	-- -- --	-- 220 nm 240 nm 260 nm	212 nm -- -- --
6.5MIN	203 nm 240 nm	-- --	204 nm 240 nm	-- --	-- no signal --	--	-- no signal --	--

MT = Methanol in tetrahydrofuran
M = Methanol
A = Asphaltene fraction
NA = Naphthene aromatic fraction

TM = Tetrahydrofuran in methanol
T = Tetrahydrofuran
PA = Polar aromatic fraction
-- = Not observed

TABLE IV: GPC DATA FOR ASPHALTS A5 AND ASF AND THEIR CORBETT FRACTIONS

Sample	LMS \pm SD %	MMS \pm SD %	SMS \pm SD %
Asphalt A5	20.9 \pm 1.2	47.2 \pm 0.5	31.9 \pm 1.6
Asphalt ASF	20.1 \pm 0.8	47.7 \pm 0.3	32.2 \pm 1.0
A5-AS	42.1 \pm 0.5	39.2 \pm 0.4	18.7 \pm 0.3
ASF-AS	27.8 \pm 0.03	44.4 \pm 0.08	27.9 \pm 0.06
A5-PA	49.3 \pm 0.1	36.7 \pm 0.4	9.2 \pm 0.2
ASF-PA	53.0 \pm 0.5	36.8 \pm 0.3	10.2 \pm 0.2
A5-NA	12.8 \pm 0.5	48.5 \pm 0.4	38.7 \pm 0.04
ASF-NA	12.6 \pm 0.03	50.1 \pm 0.1	37.3 \pm 0.2

LMS = Large molecular size
MMS = Medium molecular size
SMS = Small molecular size
AS = Asphaltene fraction

PA = Polar aromatic fraction
NA = Naphthene aromatic fraction
A5 = Virgin asphalt A5
ASF = Furfural-modified asphalt A5

HPLC CHROMATOGRAM

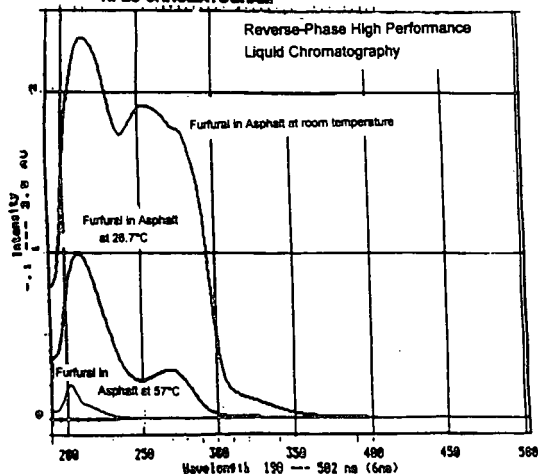


Figure 1: Wavelength spectra of furfural and asphalt for reverse-phase high performance liquid chromatography at a retention time of 4.85 min.

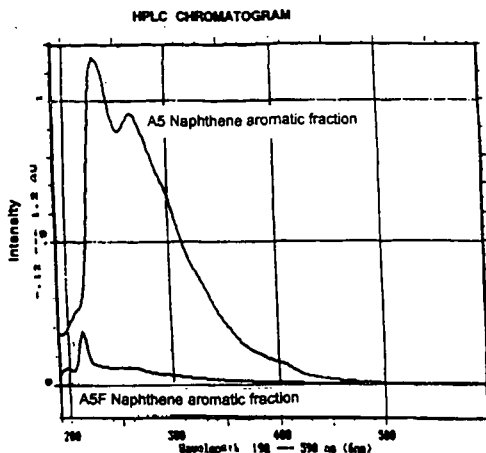


Figure 2: Ultraviolet spectra of the naphthene aromatic fraction of asphalts A5 and A5F from reverse-phase high performance liquid chromatography at a retention time of 4.7 min.

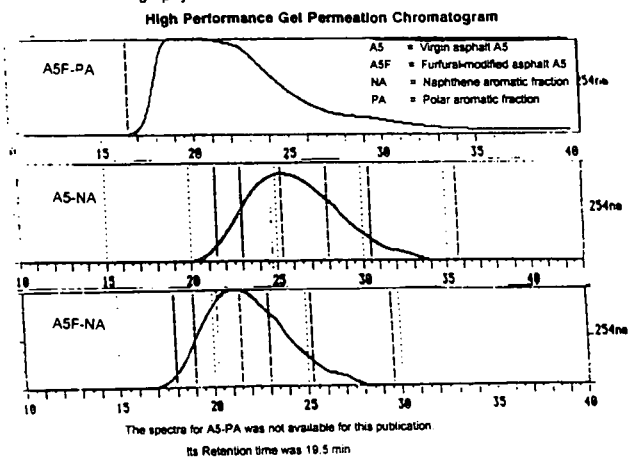


Figure 3: Chromatogram of the naphthene aromatic and polar aromatic fractions of asphalts A5 and A5F.

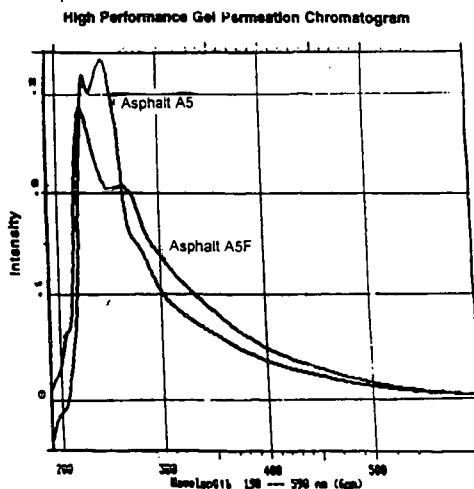


Figure 4: Ultraviolet spectra of the small molecular size polar aromatic fraction of asphalts A5 and A5F.

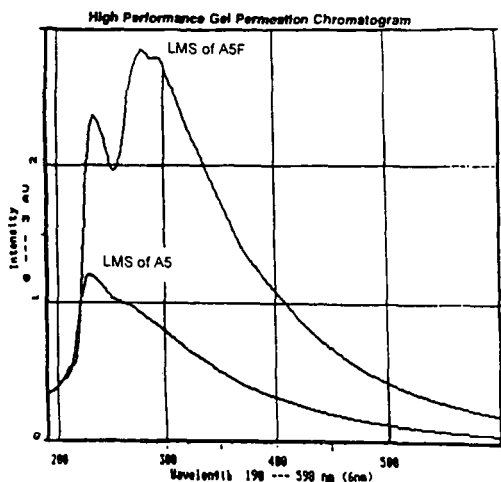


Figure 5: Ultraviolet spectra of the large molecular size polar aromatic fraction of asphalts A5 and A5F.

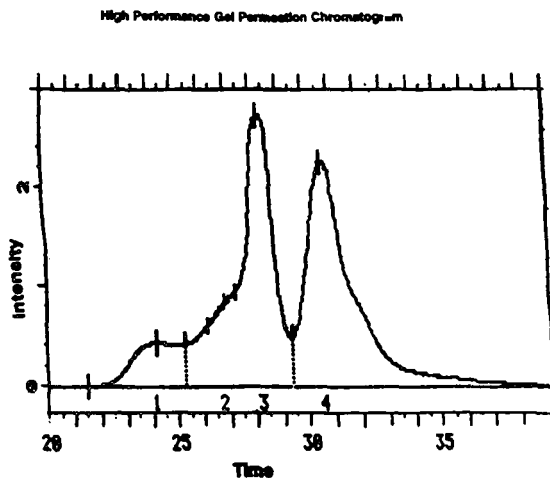


Figure 6: Chromatogram of a model polymer obtained from the reaction between phenol and furfural.

¹³C-Nuclear Magnetic Resonance Analysis

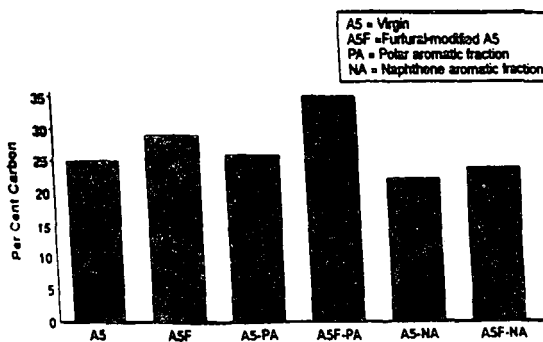


Figure 7: Nuclear Magnetic Resonance data for the percent aromatic carbon content (obtained without the Overhauser effect) present in asphalts A5 and ASF and their Corbett fractions.

¹³C-Nuclear Magnetic Resonance Analysis

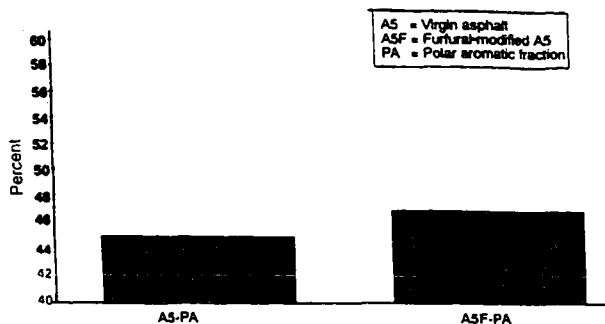


Figure 8: Nuclear Magnetic Resonance data for the percent non-protonated carbon content in polar aromatic fractions of asphalts A5 and A5F.

¹H-Nuclear Magnetic Resonance Analysis

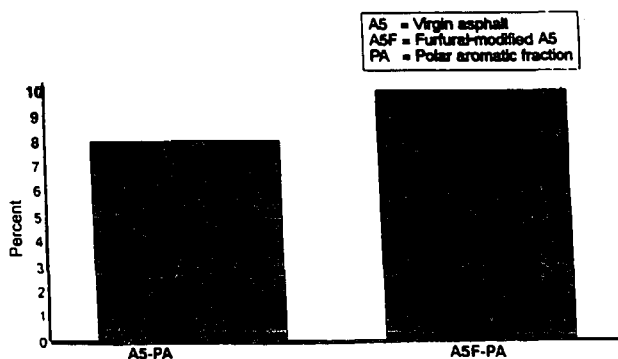
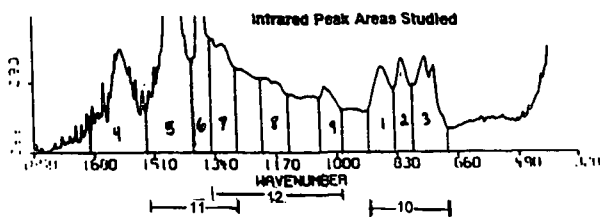


Figure 9: Nuclear Magnetic Resonance data for the aromatic to aliphatic proton ratio of the polar aromatic fractions of asphalts A5 and A5F.



Infrared Peak Area Ratios of Asphalts A5 and A5F

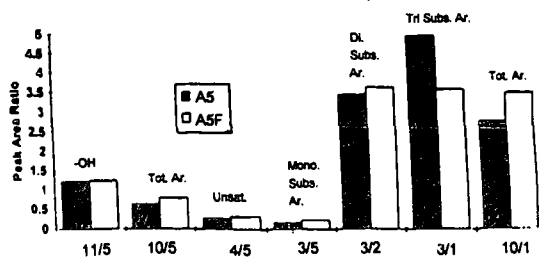


Figure 10: Infrared peak area ratios for asphalts A5 and A5F.